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(54) Title: HYDROLYSABLE AND POLYMERIZABLE OXETANE SILANE

(57) Abrégé/Abstract:

Polymerizable and hydrolysable oxetane silanes and in particular silicic acid condensates which can be prepared therefrom are described, which exhibit only a low volume shrinkage on polymerization and produce polymers with high mechanical strength and therefore can be used above all as dental material or constituent thereof.

p22 cationic init or photoinit
BF₃ ↑
[onium salts
CpFe salts (organometallics)
hexafluorophosphate]

p23 sensitizers

p24-25 dental material

p24-25 fillers

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Abstract

Polymerizable and hydrolysable oxetane silanes and in particular silicic acid condensates which can be prepared therefrom are described, which exhibit only a low volume shrinkage on polymerization and produce polymers with high mechanical strength and therefore can be used above all as dental material or constituent thereof.

Hydrolysable and polymerizable oxetane silanes

The invention relates to hydrolysable and polymerizable oxetane silanes, a process for the preparation thereof, silicic acid condensates, polymers and compositions prepared therefrom and the use of all these materials inter alia for the preparation of
5 macromolecular compositions by polymerization and for the preparation of composite materials, adhesives, coatings and in particular dental materials.

Hydrolysable silanes, which contain polymerizable organic
10 radicals, are used in the preparation of coatings, particulate fillers, adhesive compositions and monolithic moulded articles and in the surface modification of reinforcing substances. The silanes are hydrolytically condensed and polymerized thermally, photochemically or by redox initiation, i.e. cured, alone, mixed
15 with other silanes or in the presence of other metal alkoxides.

Of particular interest in connection with the preparation of organic-inorganic composite materials are above all organically modified silanes with polymerizable organic groups, such as
20 vinyl, (meth)acrylic, allyl or styryl groups, since they permit the simultaneous or consecutive formation both of an inorganic and of an organic network and therefore of composite materials with customized properties (cf H. Schmidt, Mat. Res. Soc. Symp. Proc. Vol. 32 (1984), 327-335; H. Schmidt, H. Wolter, J. Non-
25 Cryst. Solids 121 (1990) 428-435). The polymerizable silanes are as a rule in the first step hydrolytically condensed in solution. After the addition of thermal initiator or photoinitiator and removal of the solvent, nanoparticulate resins then form which are shaped and then polymerized and thus cured.

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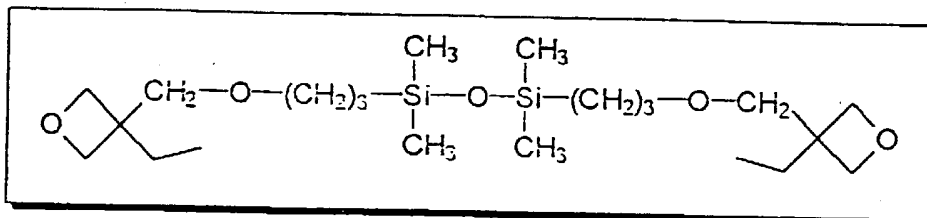
A major disadvantage of these materials, however, is that the development of the organic network which takes place on polymerization is mostly accompanied by a considerable volume contraction which may result in deformation of the moulded
35 articles, reduction in substrate adhesion, layer separation, development of voids or development of material stresses. A

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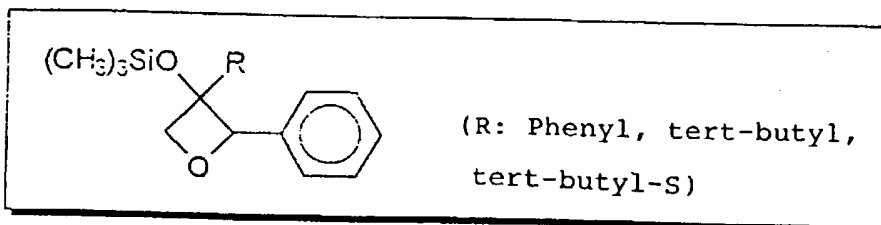
reduced volume contraction takes place with silanes which bear ring-opening groups. In this connection, EP-B-0 358 011 describes scratch-resistant materials inter alia based on 3-glycidyloxypropyl silanes, EP-B-0 486 469 describes organic-inorganic hybrid polymers of 3-glycidyloxypropyl silanes and DE-C-41 33 494 describes dental resin compositions in which e.g. silanes with ring-opening spiroortho ester groups are used. It proves to be disadvantageous, however, that epoxide silanes are toxicologically unacceptable and cationically polymerize sufficiently quickly at elevated temperatures only. Furthermore, spiroortho ester silanes exhibit only a low stability and their cationic ring-opening polymerization is generally accompanied by the formation of lactone.

Furthermore, the following silicon-containing oxetane derivatives are also known:

1. Silicon-containing oxetanes which are obtainable e.g. by hydrosilylation of 3-allyloxymethyl-3-ethyl-oxetane with 1,1,3,3-tetramethyldisiloxane (cf J.V. Crivello et al., J. Macromol. Sci.-Pure Appl. Chem. A30 (1993), 173-187):



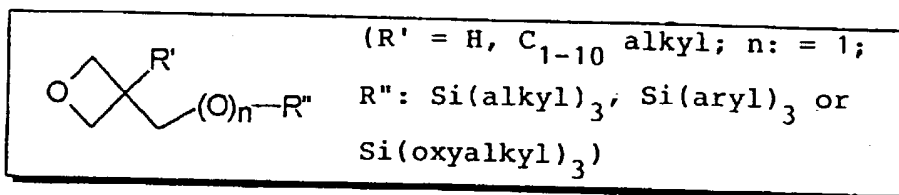
2. 3-(trimethylsiloxy)-oxetanes which can be synthesized by Paterno-Büchi reaction (cf T. Bach, Tetrahedron Lett. 32 (1991), 7037-8):



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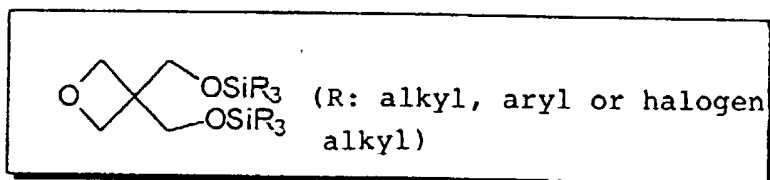
3. 3-Alkyl-3-(triorganosiloxyethyl)-oxetanes or 3-alkyl-3-(triorganosilylmethyl)-oxetanes (cf DE-A-195 06 222):

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4. 3,3-bis(triorganosiloxyethyl)-oxetanes which can be obtained by reacting 3,3-bis(hydroxymethyl)-oxetanes with appropriate triorganoaminosiloxanes R₃SiNH₂ (cf Chem. Abstr. 76 (192) 14701k):

15



It is the object of the invention to provide hydrolysable and polymerizable oxetane silanes from which, alone or together with other hydrolytically condensable and polymerizable components, stable compositions can be prepared which polymerize with only low shrinkage and at high speed at room temperature, and which are suitable as composite or coating material, adhesive or adhesion promoter or for the preparation of fillers or materials for medical or dental purposes. These silanes are to be able to be covalently incorporated into organic-inorganic composite materials and be synthetically obtainable so that the distance between silicon and the polymerizable groups can be varied.

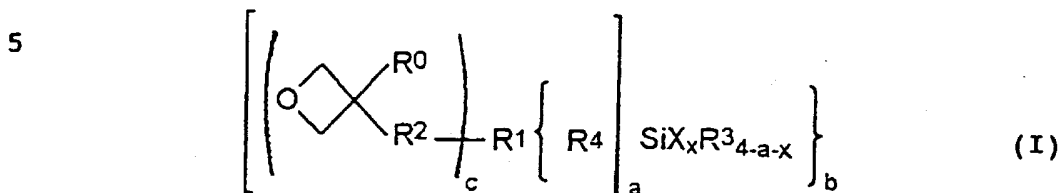
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This object is achieved according to the invention by the hydrolysable and polymerizable oxetane silanes according to Claims 1 to 3. The invention further relates to the silicic acid condensates according to Claim 4, the polymerizates according to Claim 5, the compositions according to Claims 6 and 7 and the use according to Claim 8.

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The hydrolysable and polymerizable oxetane silanes according to the invention and the stereoisomers thereof correspond to the general formula (I):



10 in which the variables R^0 , R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , X , Y , a , b , c , and x , unless otherwise stated, independently of one another have the following meanings:

- 15 R^0 = hydrogen or substituted or unsubstituted C_1 to C_{10} alkyl;
- 20 R^1 = missing or represents substituted or unsubstituted C_1 to C_{18} alkylene, C_6 to C_{18} arylene, C_7 to C_{18} alkylenearylene or arylenealkylene, these radicals being able to be interrupted by at least one group selected from ether, thioether, ester, carbonyl, amide and urethane groups;
- 25 R^2 = missing or represents substituted or unsubstituted C_1 to C_{18} alkylene, C_6 to C_{18} arylene, C_7 to C_{18} alkylenearylene or C_7 to C_{18} arylenealkylene, these radicals being able to be interrupted by at least one group selected from ether, thioether, ester, thioester, carbonyl, amide and urethane groups or being able to bear these in the terminal position;
- 30 R^3 = missing or represents substituted or unsubstituted C_1 to C_{18} alkyl, C_2 to C_{18} alkenyl, C_6 to C_{18} aryl, C_7 to C_{18} alkylaryl or C_7 to C_{18} arylalkyl, these radicals being able to be interrupted by at least one group selected from
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ether, thioether, ester, carbonyl, amide and urethane groups;

R^4 = missing or represents substituted or unsubstituted $-\text{CHR}^6-\text{CHR}^6-$, $-\text{CHR}^6-\text{CHR}^6-\text{S}-\text{R}^5$, $-\text{S}-\text{R}^5-$, $\text{Y}-\text{CO}-\text{NH}-\text{R}^5-$ or $-\text{CO}-\text{O}-\text{R}^5-$;

R^5 = substituted or unsubstituted C_1 to C_{18} alkylene, C_6 to C_{18} arylene, C_6 to C_{18} alkylenearylene or C_6 to C_{18} arylenealkylene, these radicals being able to be interrupted by at least one group selected from ether, thioether, ester, carbonyl, amide and urethane groups;

R^6 = hydrogen or substituted or unsubstituted C_1 to C_{18} alkyl or C_6 to C_{10} aryl;

X = a hydrolysable group, namely halogen, hydroxy, alkoxy or acyloxy;

Y = O or S;

a = 1, 2 or 3;

b = 1, 2 or 3;

c = 1 to 6; and

x = 1, 2 or 3;

and with the proviso that

(i) $a+x = 2, 3$ or 4

and

(ii) a and/or $b = 1$.

However, the above formula covers only those compounds which are compatible with the valency theory.

The silanes according to the invention are usually present as stereoisomer mixtures and in particular as racemates.

The ether, thioether, ester, thioester, carbonyl, amide and urethane groups which are possibly present in the radicals are defined by the following formulae: $-\text{O}-$, $-\text{S}-$, $-\text{CO}-\text{O}-$, $-\text{O}-\text{CO}-$, $-\text{CO}-\text{S}-$, $-\text{S}-\text{CO}-$, $-\text{CS}-\text{O}-$, $-\text{O}-\text{CS}-$, $-\text{CO}-$, $-\text{CO}-\text{NH}-$, $-\text{NH}-\text{CO}-$, $-\text{O}-\text{CO}-\text{NH}-$ and $-\text{NH}-\text{CO}-\text{O}-$.

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The non-aromatic radicals or non-aromatic parts of the radicals possible in formula (I) can be straight-chained, branched or cyclic.

- 5 Alkyl radicals have preferably 1 to 8 and particularly preferably 1 to 4 carbon atoms. Particular examples of possible alkyl radicals are methyl, ethyl, n- and iso-propyl, sec- and tert-butyl, n-pentyl, cyclohexyl, 2-ethylhexyl and octadecyl.
- 10 Alkenyl radicals have preferably 2 to 10 and particularly preferably 2 to 6 carbon atoms. Particular examples of possible alkenyl radicals are vinyl, allyl and iso-butenyl.

Preferred examples of possible aryl radicals are phenyl, biphenyl
15 and naphthyl.

Alkoxy radicals preferably have 1 to 6 carbon atoms. Particular examples of possible alkoxy radicals are methoxy, ethoxy, n-propoxy, iso-propoxy and tert-butoxy.

20 Acyloxy radicals preferably have 2 to 5 carbon atoms. Particular examples are acetyloxy and propionyloxy.

Preferred alkylene radicals are derived from the above preferred
25 alkyl radicals and preferred arylene radicals are derived from the above preferred aryl radicals.

Preferred radicals consisting of a combination of non-aromatic and aromatic parts, such as alkylaryl, arylalkyl, alkylenearylene
30 and arylenealkylene radicals, are derived from the above preferred alkyl and aryl radicals. Particular examples thereof are benzyl, 2-phenylethyl and tolyl.

The mentioned substituted R radicals bear one or more simple
35 substituents. Examples of these substituents are methyl, ethyl, phenyl, benzyl, hydroxymethyl, hydroxyethyl, methoxy, ethoxy,

- 7 -

chloro, bromo, hydroxy, mercapto, isocyanato, vinyloxy, acryloxy, methacryloxy, allyl, styryl, epoxy, carboxyl, SO_3H , PO_3H_2 or PO_4H_2 .

For a, b, c or $x \geq 2$, the radicals X and the individual R radicals can in each case have the same or a different meaning.

Moreover, preferred definitions exist for the above-stated variables of formula (I) which, unless otherwise stated, can be chosen independently of one another and are as follows:

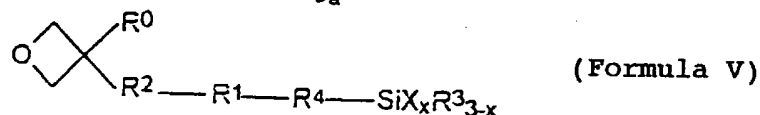
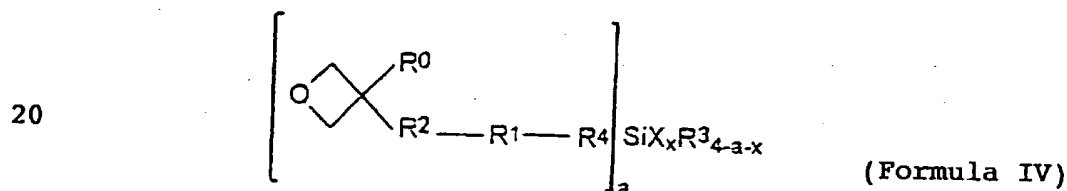
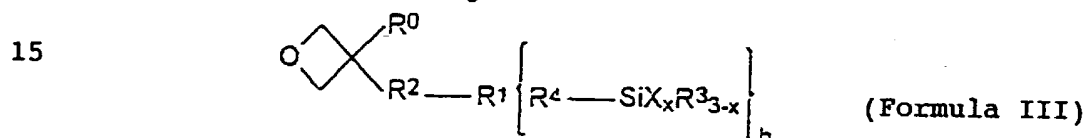
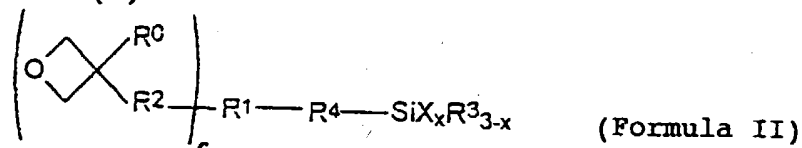
- 10 R^0 = hydrogen or C_1 to C_3 alkyl;
 R^1 = C_1 to C_8 alkylene, these radicals being able to be interrupted by at least one group selected from ether, thioether, ester and urethane groups;
 15 R^2 = missing or represents C_1 to C_8 alkylene, these radicals being able to be interrupted by at least one group selected from ether, thioether, ester, thioester, carbonyl, amide and urethane groups or being able to bear these in the terminal position;
 20 R^3 = missing or represents methyl, ethyl or phenyl;
 R^4 = missing or represents $-\text{CHR}^6-\text{CHR}^6-$, $-\text{S}-\text{R}^5-$, $-\text{Y}-\text{CO}-\text{NH}-\text{R}^5-$ or $-\text{CO}-\text{O}-\text{R}^5-$;
 R^5 = C_1 to C_8 alkylene, these radicals being able to be interrupted by at least one group selected from ether, thioether, ester, carbonyl, amide and urethane groups;
 25 R^6 = hydrogen or C_1 to C_3 alkyl;
 X = methoxy, ethoxy or chloro;
 30 Y = O or S;
 a = 1;
 b = 1;
 c = 1 to 6;
 x = 2 or 3; and/or
 35 a+x = 3.

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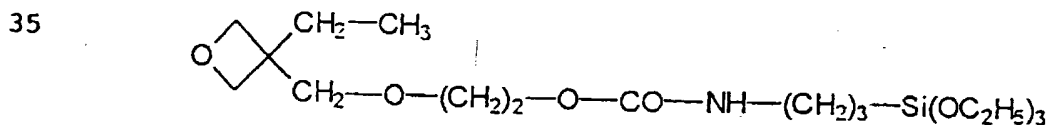
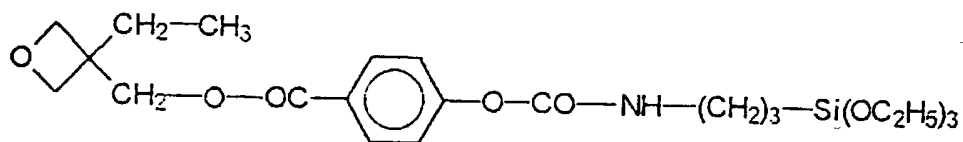
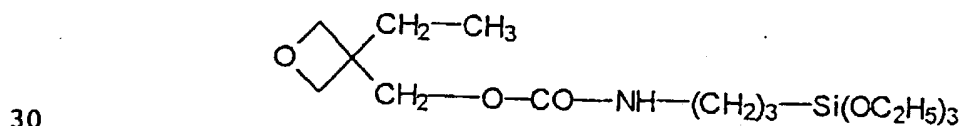
The individual R radicals can in turn bear simple substituents.

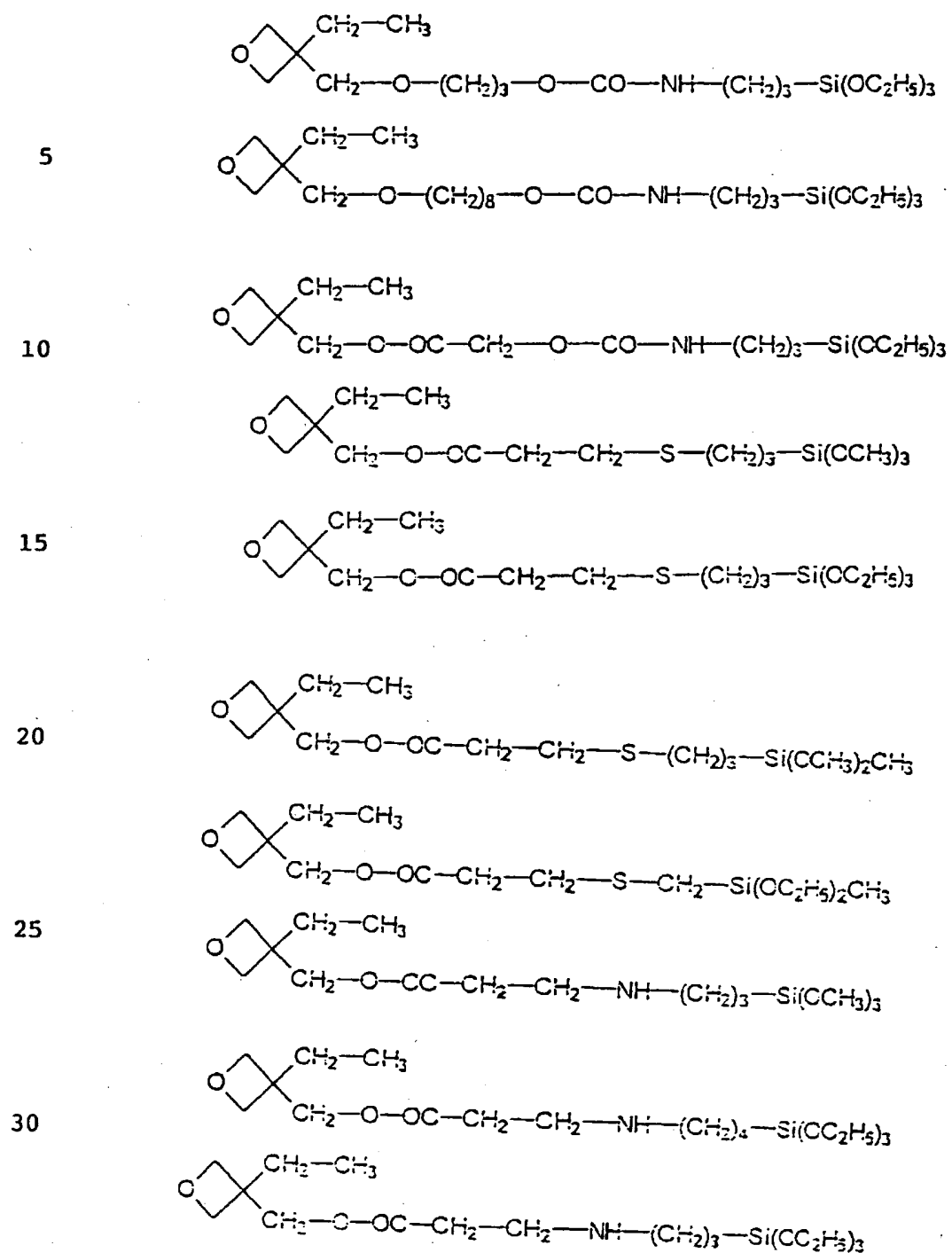
Preferred compounds are accordingly those in which at least one of the variables of formula (I) has the above-described preferred definition.

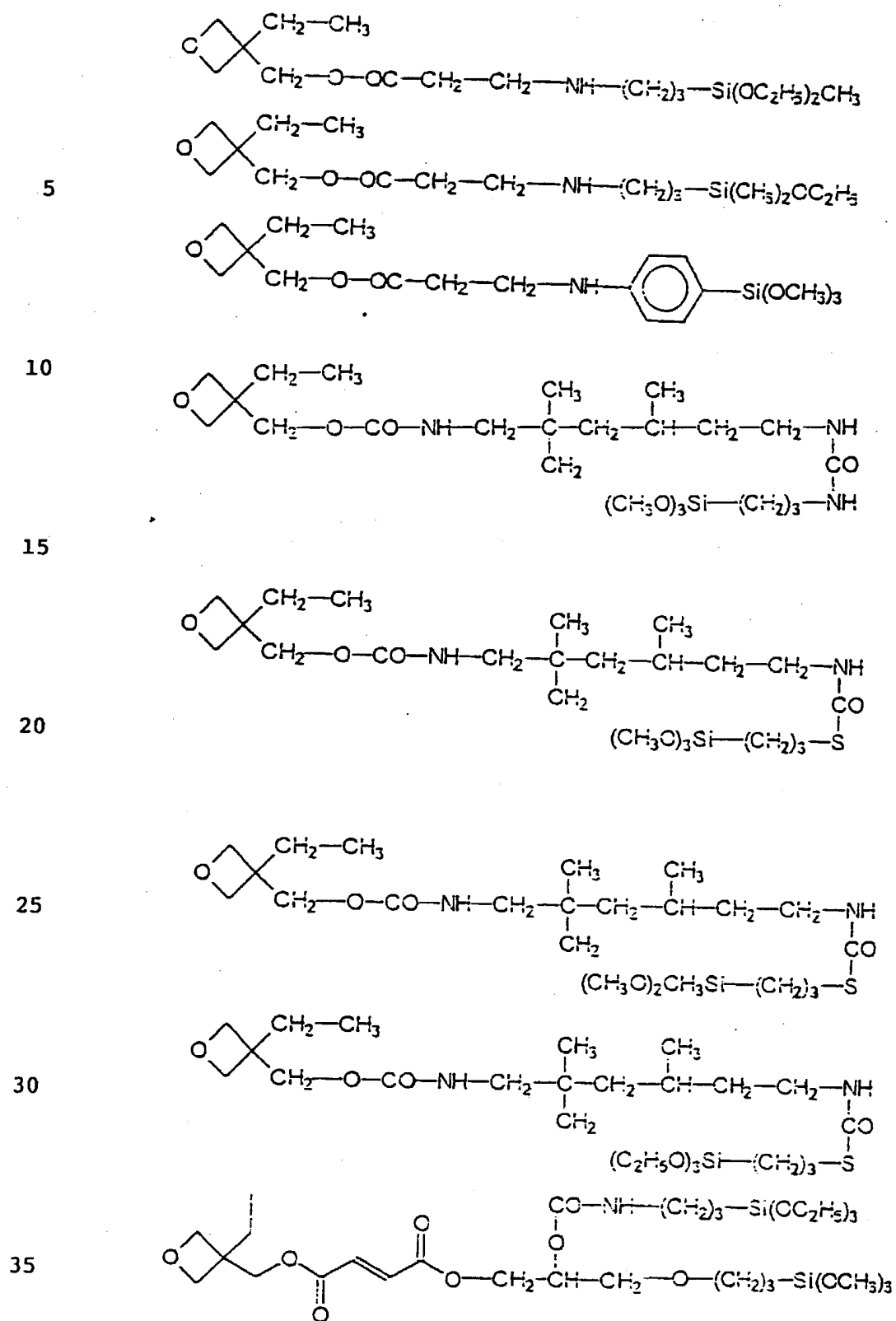
Furthermore, those oxetane silanes of formula (I) are preferred in which the indices a, b and/or c have the value 1, and examples thereof are the silanes according to the general formulae (II), (III), (IV) and (V) below.



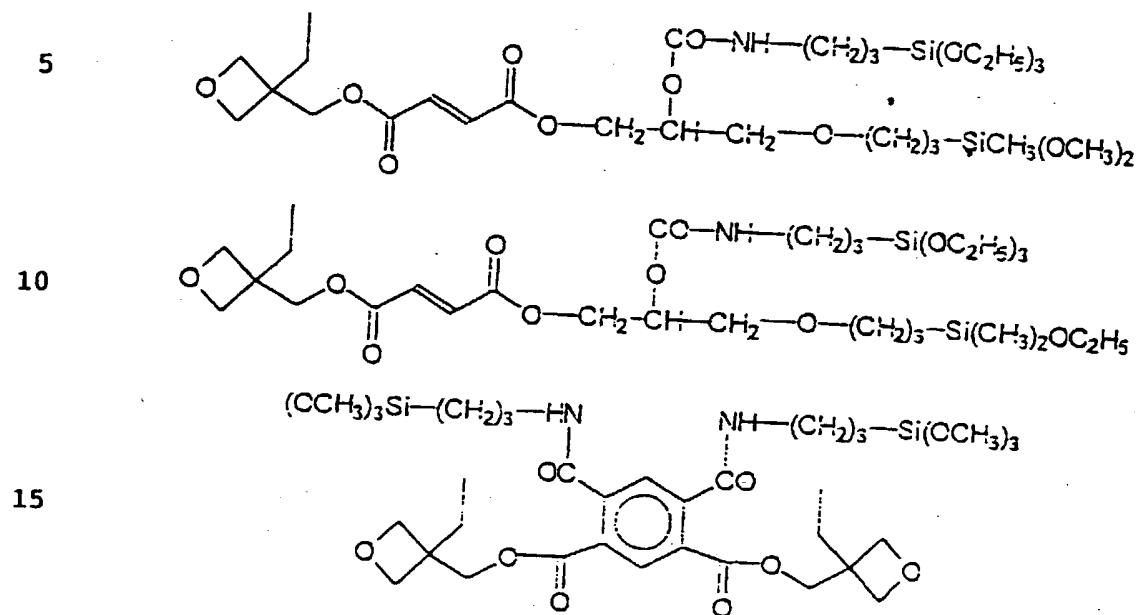
Particular examples of preferred oxetane silanes according to the invention of formula (I) are given below:







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25 The preparation of the oxetane silanes (I) according to the invention is possible in particular via a large number of conventional addition or condensation reactions which are carried out according to the methods customary for these reactions. Processes which can be used for preparing the silanes according to the invention are described e.g. in W. Noll, Chemie und

30 Technologie der Silicone, 2nd edition, Verlag Chemie, Weinheim 1968, in particular p. 22 et seq., and in the review by R.C. Mehrotra in J. Non-Crystalline Solids 100, (1988) 1-15 and the literature quoted in this article.

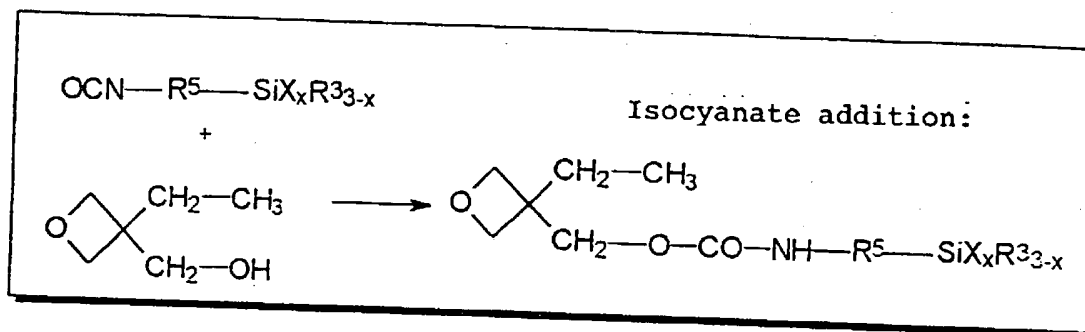
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In a first variant, e.g. 3-ethyl-3-hydroxymethyl oxetane (1) can be added to an isocyanate group-containing silane:

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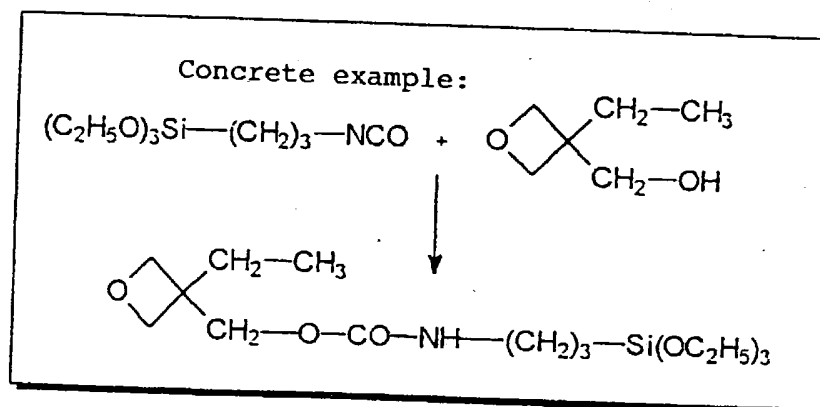
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Furthermore, starting from 3-acryloyloxymethyl-3-ethyloxetane (2), e.g. the thiol-ene addition with mercaptosilanes is possible:

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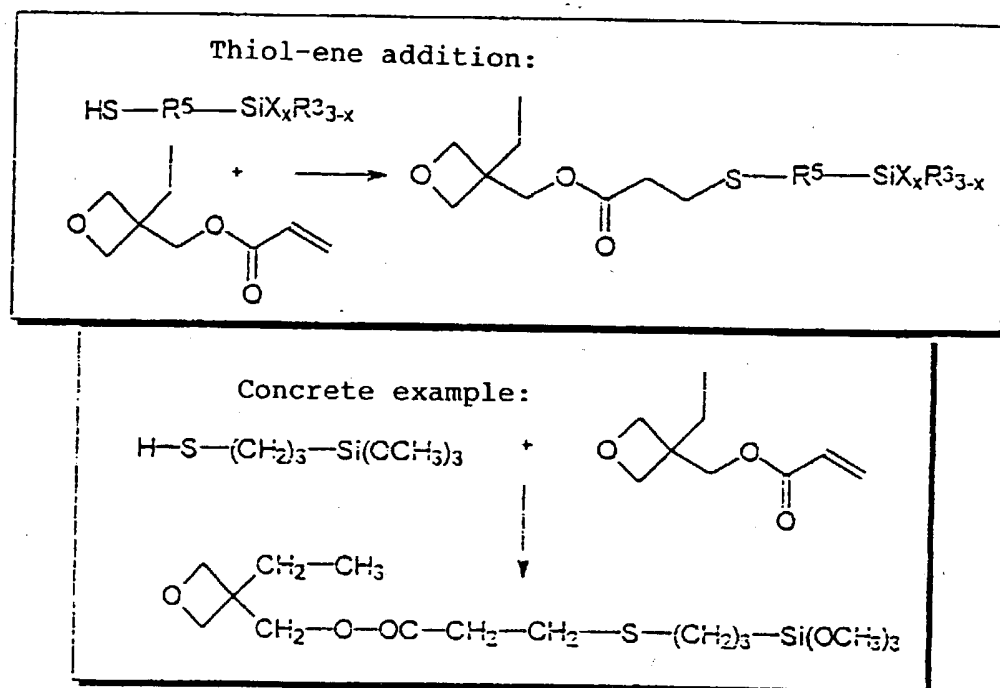
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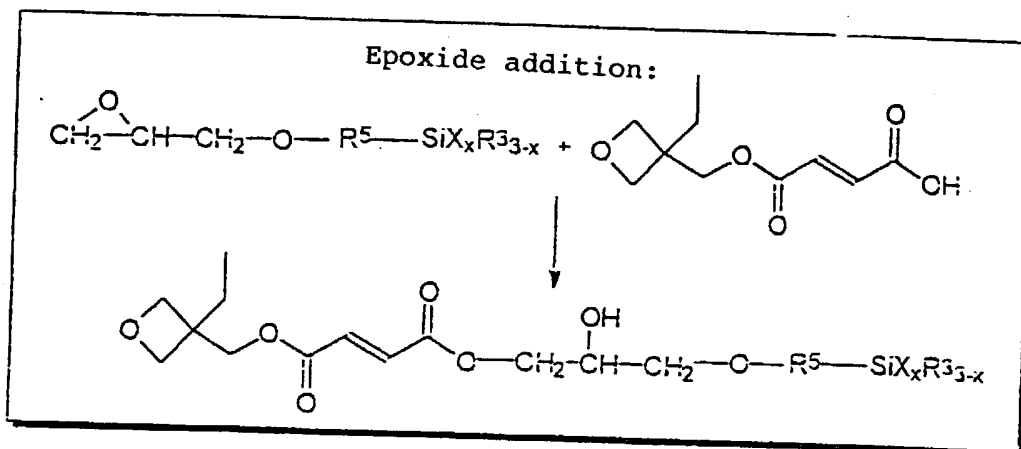
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Moreover, the semi-ester of fumaric acid and 3-ethyl-3-hydroxymethyl-oxetane can be added to an epoxide silane:

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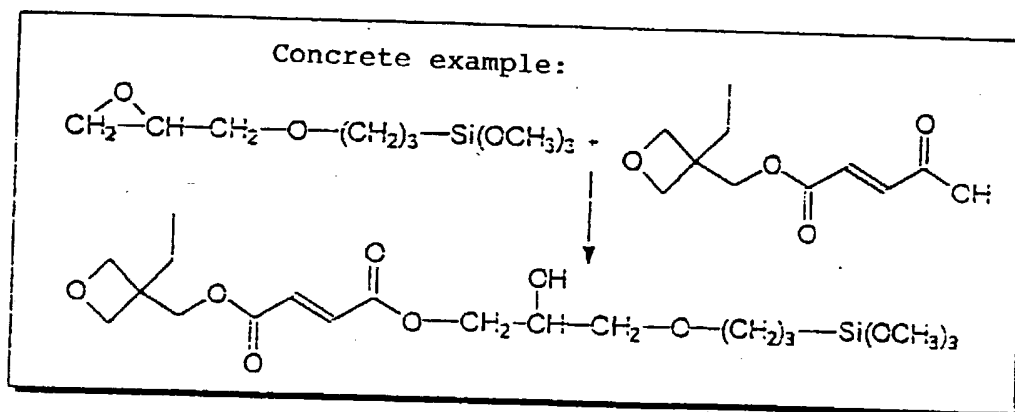
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The silane obtained can be reacted further with an isocyanate group-containing silane, so that oxetane silanes with two silyl groups are obtained:

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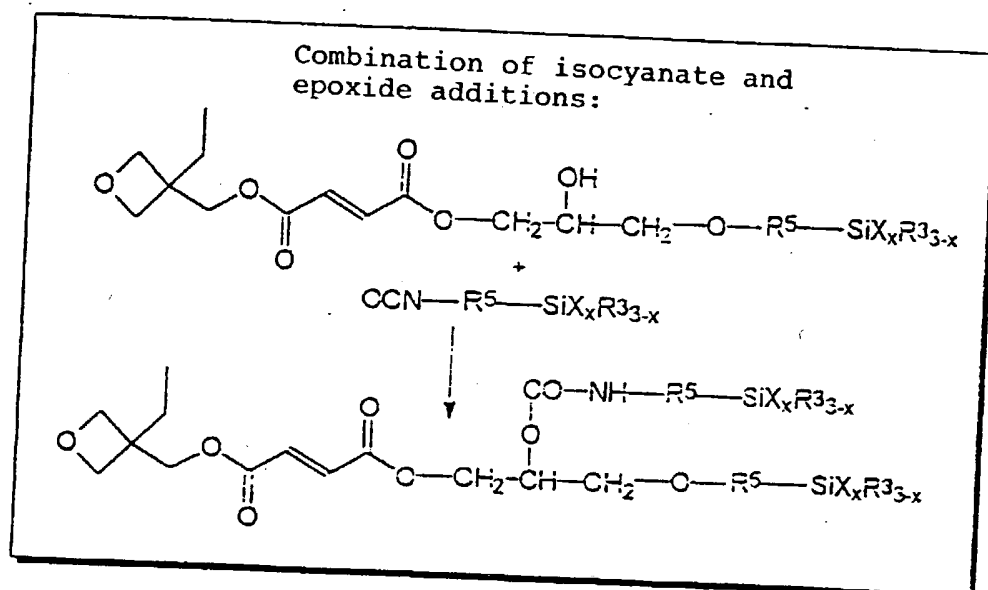
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Silanes with several oxetane radicals are accessible via addition reactions. Thus, e.g. by reacting (1) with tetracarboxylic acid dianhydrides, such as pyromellitic acid anhydride, 1,2,3,4-butanetetracarboxylic acid dianhydride or tetrahydrofuran-2,3,4,5-tetracarboxylic acid dianhydride, an adduct can be obtained which is further reacted with 1 or 2 mol of an epoxide or isocyanatosilane.

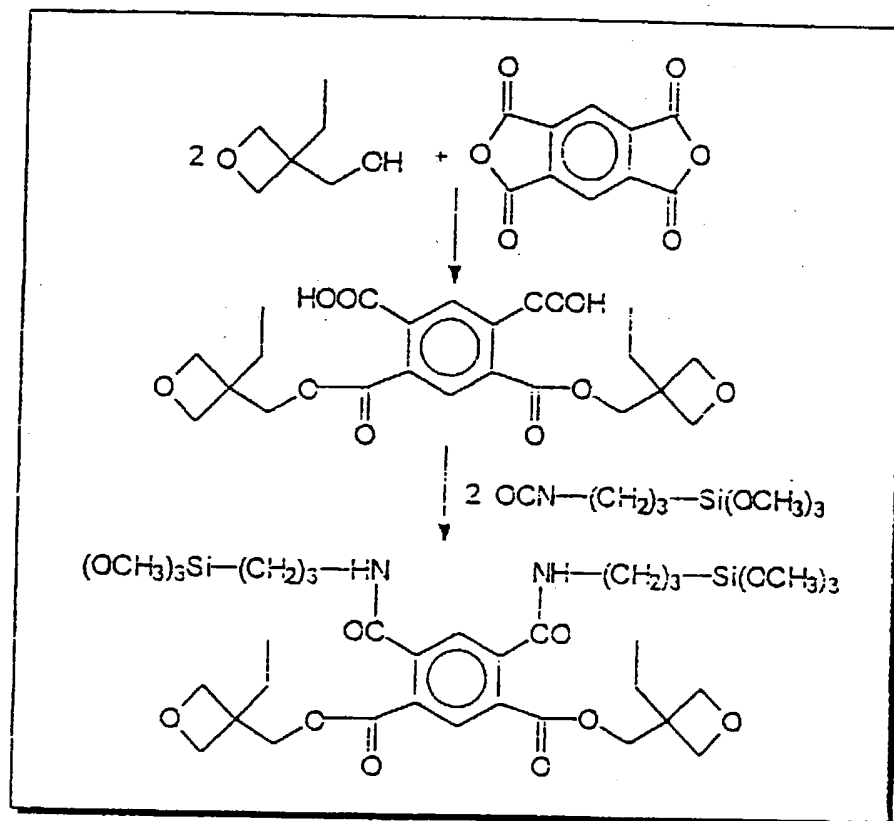
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The silanes (I) according to the invention are polymerizable via the oxetane groups and hydrolysable via the radicals X. The polymerization of the oxetane groups leads to the formation of an organic network, whereas the hydrolysable groups produce an inorganic polysiloxane network through polycondensation.

The oxetane silanes according to the invention are substances of high reactivity which on hydrolysis form polymerizable silicic acid condensates which can be polymerized in the presence of usual cationic initiators or photoinitiators at room temperature or under irradiation with light of the visible or UV range to form mechanically stable layers, moulded articles or fillers.

The number of hydrolysable groups, polymerizable groups and further functional groups can be varied by suitable selection of the starting materials used in the preparation of the oxetane silanes. Depending on the type and number of the hydrolysable groups, e.g. alkoxy groups, and on the number of oxetane groups, the condensation of the oxetane silanes and the polymerization of the obtained condensates therefore results in materials with properties which range from silicone rubber-like to glass-like. In comparison with radically polymerizable silanes, no inhibition layer forms on polymerization of the oxetane silanes according to the invention, which is very advantageous especially in the preparation of coatings.

The development of a three-dimensional, organic network is possible when at least two oxetane radicals are present, the mechanical properties, such as e.g. strength and flexibility, and the physico-chemical properties, e.g. adhesiveness, water absorption and refractive index, of the obtained silicic acid condensates being variable and optimally adaptable to the requirements of the respective case of application via the distance between the Si atom and the oxetane radical, i.e. via the length of the spacer group, and by incorporation of further functional groups. Aliphatic groups result in products which are

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rather flexible, and aromatic groups result in products which are rather rigid.

Furthermore, the crosslinking density, which then likewise
5 influences the properties and possible applications of the
corresponding silicic acid condensates, can be set by means of
the number of polymerizable oxetane groups. Moreover, if the
oxetane silanes according to the invention also contain ionically
10 crosslinkable groups such as e.g. (meth)acrylate, styryl or
allyl, then a further increase in crosslinking density can be
achieved simultaneously or consecutively, i.e. as a 2-stage
process, by their radical polymerization.

The oxetane silanes according to the invention and their silicic
15 acid condensates possess only a low volatility, with the result
that they can be processed in an easy and largely harmless
manner. In view of the above-stated variation possibilities of
the condensable and polymerizable radicals of the oxetane silanes
according to the invention, silicic acid condensates which can
20 be prepared therefrom can be provided as resins or fillers for
very different areas of application.

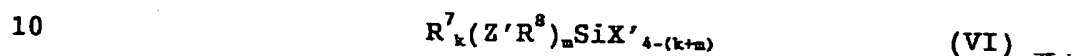
The silanes (I) are stable compounds which can be processed
either alone or together with other hydrolysable, condensable
25 and/or polymerizable components to form the silicic acid
condensates according to the invention.

In addition to the silanes of formula (I), other hydrolytically
condensable compounds of silicon, aluminium, titanium, zirconium
30 or phosphorus can be used in the preparation of the silicic acid
condensates according to the invention, which are then also
referred to as silicic acid (hetero)condensates. These compounds
can be used either as such or in already precondensed form. It
is preferred that at least 20 mol.%, particularly preferably at
35 least 80 mol.%, based on monomeric compounds, of hydrolysable
silicon compounds are used for the preparation of the silicic

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acid (hetero)condensates according to the invention. It is also preferred that at least 10 mol.%, in particular 40 to 100 mol.%, in each case based on monomeric compounds, of oxetane silanes according to the invention are used for the preparation of the
5 silicic acid (hetero)condensates.

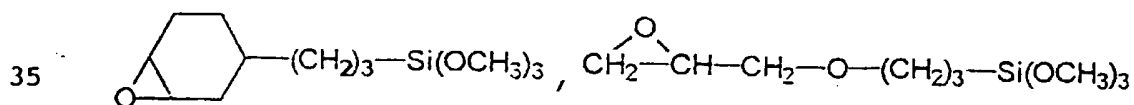
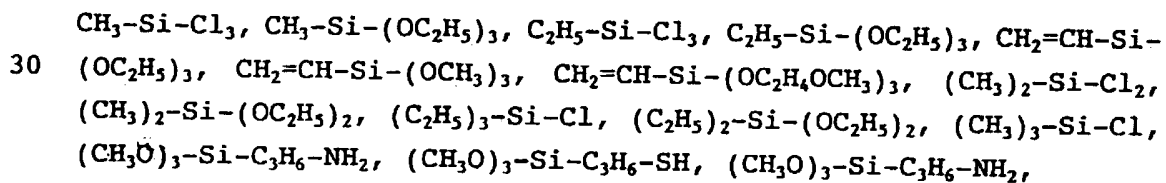
Preferably at least one silane of the general formula (VI) is used as other hydrolytically condensable compounds:



in which R^7 , Z' , R^8 , X' , k and m , unless otherwise stated, independently of one another have the following meanings:

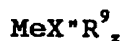
- 15 R^7 = C_1 to C_8 alkyl, C_2 to C_{12} alkenyl or C_6 to C_{14} aryl;
 R^8 = C_1 to C_8 alkylene, C_2 to C_{12} alkenylene or C_6 to C_{14} arylene;
 X' = hydrogen, halogen or C_1 to C_8 alkoxy;
 Z' = mercapto, glycidyl, acrylic, methacrylic, vinyl, allyl
20 or vinyl ether group;
 k = 0, 1, 2 or 3;
 m = 0, 1, 2 or 3; and
 $k+m$ = 1, 2 or 3.

- 25 Such silanes are described e.g. in DE-C-34 07 087, and particular examples of hydrolytically condensable silanes of general formula (VI) are:



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Furthermore, at least one zirconium, titanium or aluminium compound of the formulae



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can be used as other preferred hydrolytically condensable compounds, in which Me, R^9 , R^{10} , X^n , y and z independently of one another have the following meanings:

- 10 Me = Zr or Ti;
 R^9 = hydrogen, substituted or unsubstituted C_1 to C_{12} alkyl, C_7 to C_{15} alkylaryl or C_6 to C_{14} aryl;
 R^{10} = halogen, OH, C_1 to C_8 alkoxy;
 X^n = halogen, OH, C_1 to C_8 alkoxy;
 15 y = 1 to 4, in particular 2 to 4;
 z = 1 to 3, in particular 0 to 2.

- Preferred examples of zirconium and titanium compounds which can be used are ZrCl_4 , $\text{Zr}(\text{OC}_2\text{H}_5)_4$, $\text{Zr}(\text{OC}_3\text{H}_7)_4$, $\text{Zr}(\text{OC}_4\text{H}_9)_4$, ZrOCl_2 , TiCl_4 ,
 20 $\text{Ti}(\text{OC}_2\text{H}_5)_4$, $\text{Ti}(\text{OC}_3\text{H}_7)_4$ and $\text{Ti}(\text{OC}_4\text{H}_9)_4$. Preferred examples of aluminium compounds which can be used are $\text{Al}(\text{OCH}_3)_3$, $\text{Al}(\text{OC}_2\text{H}_5)_3$, $\text{Al}(\text{OC}_3\text{H}_7)_3$, $\text{Al}(\text{OC}_4\text{H}_9)_3$ and AlCl_3 .

- Complexed Zr, Ti and Al compounds can also be used, in which
 25 inter alia acids or β -dicarbonyl compounds can act as complexing agents.

- Other hydrolysable compounds which can be used for preparing the silicic acid (hetero)condensates are e.g. boron trihalides, tin
 30 tetrahalides, tin tetraalkoxides and vanadyl compounds.

- The silicic acid condensates according to the invention of the silanes (I) are obtained by hydrolysis of the hydrolysable groups X present, e.g. alkoxy groups, and by subsequent condensation,
 35 which results in the formation of an inorganic network of Si-O-Si units. The hydrolysis and condensation usually take place in

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basic or acidic medium, a linking of C=C double bonds which are contained in the silanes used being generally undesired.

The silicic acid condensates according to the invention can also
5 be present in incompletely hydrolysed and condensed form. In such cases, they are referred to as so-called precondensates.

The customary procedure in the preparation of the silicic acid (hetero)condensates according to the invention is that the
10 silanes (I), optionally dissolved in a solvent, are reacted at room temperature or with slight cooling and in the presence of a hydrolysis and condensation catalyst with the necessary quantity of water, and the resulting mixture is stirred for one to several hours. Coming into consideration as solvents are
15 above all aliphatic alcohols, such as e.g. ethanol or i-propanol, dialkyl ketones, such as acetone or methyl isobutyl ketone, ethers, such as diethyl ether or tetrahydrofuran (THF), esters, such as ethyl or butyl acetate, and mixtures thereof.

20 If the hydrolytic condensation is carried out in the presence of reactive Zr, Ti or Al compounds, the addition of water should take place in stages at ca 0 to 30°C. It is usually favourable not to add water as such, but to introduce it in the form of water-containing solvents, such as aqueous ethanol, or by release
25 via a chemical reaction, such as via an esterification.

The hydrolysis and condensation preferably takes place in the presence of a condensation catalyst, preference being given to proton- or hydroxyl ion-releasing compounds such as organic or
30 inorganic acids or bases. Particularly preferred are volatile acids or bases, in particular hydrochloric acid or ammonia. It has proved to be worthwhile for hydrolysis and condensation to adopt procedures of sol-gel technology, as are described e.g. in C.J. Brinker et al., "Sol-Gel Science", Academic Press, Boston,
35 1990. The "sol-gel process" is also disclosed in DE-A-27 58 414,

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DE-A-27 58 415, DE-A-30 11 761, DE-A-38 26 715 and DE-A-38 35 968.

The obtained silicic acid (hetero)condensates of the silanes (I) and optionally of other hydrolytically condensable compounds can be used either as such or after partial or complete
 5 removal of the solvent used. In some cases, it can also prove to be advantageous to replace the solvent used for the hydrolytic condensation with another solvent.

The polymerizable silicic acid (hetero)condensates according to the invention and the silanes (I) and compositions containing these condensates or silanes can be cured by cationic
 10 polymerization or photopolymerization, the polymerization usually taking place after suitable initiators and other polymerizable components have been added. If different polymerizable groups, e.g. oxetane and (meth)acrylic groups, are present, several curing mechanisms, e.g. cationic and radical polymerization, can be used simultaneously or in successive stages.

15 Cationic initiators and/or photoinitiators are preferably used to initiate the cationic polymerization.

Preferred examples of cationic initiators are strong Brönsted and Lewis acids, e.g. sulphuric acid, trifluoroacetic acid, aluminium trichloride or boron trifluoride.

Suitable photoinitiators are onium salts, triarylsulphonium salts, diaryliodonium salts, cyclopentadienyl iron (I) salts and isoquinoline salts. Particularly suitable is a mixture of 4-
 (diphenylsulphino)-phenylphenylsulphide-bis-hexafluoroantimonate and bis[4-
 (diphenylsulphino)-phenyl]sulphide-hexafluoroantimonate (CYRACURE™ UVI 6974
 25 photoinitiator; CYRACURE is a trade-mark of Union Carbide Corporation), bis[4-
 (diphenylsulphino)-phenyl]sulphide hexafluorophosphate (DEGACURE™ K1-85
 photoinitiator; DEGACURE is a trade-mark of Degussa Aktiengesellschaft Joint Stock Company), diphenyliodonium hexafluoroantimonate or hexafluorophosphate, and (η^5 -2,4-
cyclopentadien-1-yl)[1,2,3,4,5,6- η](cumene)-iron(I)-

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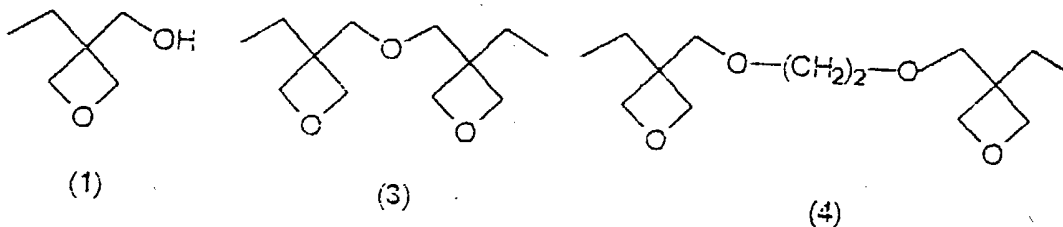
hexafluorophosphine complex (IRGACURE™ 261 photoinitiator; IRGACURE is a trademark of Ciba-Geigy Corporation). The sensitivity can be increased in the visible range by

5 sensitizers, such as thioxanthone derivatives, camphor quinone, phenanthrenequinone or perylene. Furthermore, it also proves to be advantageous to carry out the photopolymerization in the presence of radical photoinitiators, such as e.g. benzoin alkyl ethers, benzil dialkyl ketals or acrylic phosphine oxides.

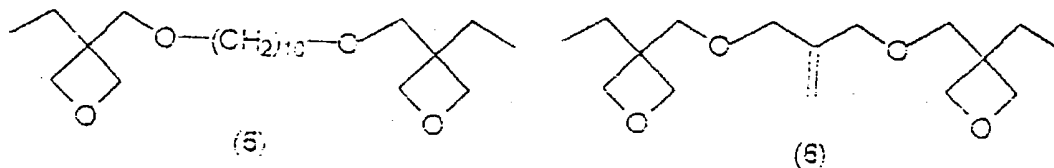
10 In the compositions according to the invention, suitable polymerizable mono- or multifunctional monomers which are also referred to as diluent monomers can also be present in addition to the silanes (I) or the corresponding silicic acid (hetero)condensates.

Particularly suitable diluent monomers are oxetane group-containing monomers, such as 3-ethyl-3-hydroxymethyloxetane (1), 3,7-bis(3-oxetanyl)-5-oxa-nonane (3), 3,3'-(1,2-ethanediylbis(oxymethylene))-bis(3-ethyloxetane) (4), 3,3'-(1,10-decanediylbis(oxymethylene))-bis(3-ethyloxetane) (5), 3,3'-(1,3-(2-methylenyl)propanediylbis(oxymethylene))-bis(3-ethyloxetane) (6) or 3,3'-(1,4-xylenediylbis(oxymethylene))-bis(3-ethyloxetane) (7):

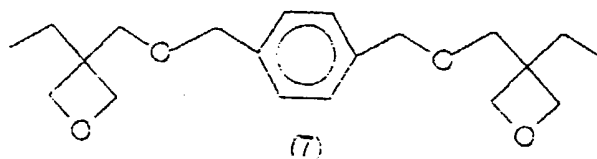
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These compounds are known (cf H. Sasaki, J.V. Crivello, J. Macromol. Sci.-Pure Appl. Chem. A29 (1992) 915-930; J.V. Crivello, H. Sasaki, J. Macromol. Sci.-Pure Appl. Chem. A30 (1993) 189-206).

5

Moreover, radically polymerizable diluent monomers such as monofunctional (meth)acrylates, e.g. methyl (meth)acrylate, ethyl (meth)acrylate, butyl (meth)acrylate, benzyl (meth)acrylate, furfuryl (meth)acrylate or phenyl (meth)acrylate, and
10 polyfunctional (meth)acrylates, e.g. bisphenyl-A-di(meth)acrylate, bis-GMA (an addition product of methacrylic acid and bisphenol-A-diglycidyl ether), UDMA (an addition product of 2-hydroxyethyl methacrylate and 2,2,4-hexamethylene diisocyanate), di-, tri- or tetraethylene glycol
15 di(meth)acrylate, decanediol di(meth)acrylate, trimethylolpropane tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, butanediol di(meth)acrylate, 1,10-decanediol di(meth)acrylate or 1,12-dodecanediol di(meth)acrylate, can also be used.

20 The silanes according to the invention, the silicic acid condensates or silicic acid heterocondensates thereof and compositions containing them can be used as such or in at least partially polymerized form as varnishes for coating plastics, glass or other substrates, as fillers or bulk material for
25 composites and for producing medical materials such as contact lenses. They are, however, particularly preferably used as dental material or a constituent thereof.

The compositions according to the invention can also optionally
30 contain other additives, such as e.g. coloring agents (pigments or dyes), stabilizers, flavorants, microbiocidal active ingredients, flameproofing agents, plasticizers or UV absorbers.

Other preferred additives are fillers. Examples of preferred
35 fillers are quartz, glass ceramic or glass powders, in particular barium or strontium silicate glass powder, lithium-aluminium

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silicate glass powder, silicon, zirconium or aluminium oxides, or mixtures thereof, finely divided silicas, in particular pyrogenic or precipitated silicas, and X-ray-opaque fillers, such as e.g. ytterbium trifluoride.

5

A particularly preferred composition according to the invention contains:

- 10 (a) 5 to 90, in particular 10 to 70 wt.%, relative to the composition, of silicic acid (hetero)condensate of a silane (I),
- (b) 0 to 80, in particular 0 to 50 wt.%, relative to the composition, of diluent monomer,
- 15 (c) 0.1 to 5, in particular 0.2 to 2.0 wt.%, relative to the composition, of polymerization initiator, and/or
- (d) 0 to 90, in particular 0 to 80 wt.%, relative to the composition, of fillers.

20 The compositions according to the invention are particularly preferably used as dental cement, dental filling material or dental bonding for filling materials. The compositions are used in particular by applying them to the area of a false or natural tooth to be treated and curing by polymerization.

25 It proves to be a particular advantage of the compositions according to the invention that on the one hand they exhibit only a low polymerization shrinkage and on the other hand they result in composite materials with high mechanical strength. Such a combination of properties is of particular significance

30 especially in the case of dental materials.

The invention is explained in more detail below with reference to examples.

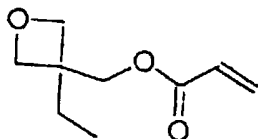
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Example 1: Synthesis of 7-trimethoxysilyl-4-thia-heptanoic acid-(3-ethyl-oxetan-3-yl)methyl ester (8)

1st stage: 3-ethyloxetan-3-yl-methyl acrylate

5



62.3 g (688 mmol) of acrylic acid chloride in 300 ml of diethyl
 10 ether were added dropwise to an ice-cooled solution of 80 g (688 mmol) of 3-ethyl-3-hydroxyethyl-oxetane and 77.3 g of collidine (688 mmol) in 400 ml of diethyl ether. After 6 hrs' stirring at room temperature, the formed hydrochloride was filtered off, and the filtrate was washed with aqueous hydrochloric acid and with
 15 NaHCO₃ solution. After drying with anhydrous Na₂SO₄ and additional stabilizing with hydroquinone monomethyl ether, the solvent was drawn off at 120 mbar in a rotary evaporator. After fractional distillation (b.p._{0.2}:56°C), 57 g (50% yield) of a colourless, clear liquid were obtained.

20

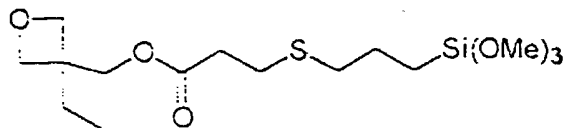
¹H-NMR: 5.6-6.6 (m, 3H, CH=CH₂), 3.4-4.7 (m, 6H, CH₂O),
 1.6-1.9 (q, 2H, CH₂), 0.7-1.0 (t, 3H, CH₃) ppm.

IR (Film): 2965, 2874, 1728, 1408, 1268, 1194 cm⁻¹.

25

2nd stage: 7-trimethoxysilyl-4-thia-heptanoic acid-(3-ethyl-oxetan-3-yl)methyl ester)

30



(8)

17.0 g (0.1 mol) of 3-ethyl-oxetan-3-yl-methyl acrylate were
 added in a dry and argon-flushed apparatus to 19.6 g (0.1 mol)
 of 3-mercaptopropyl-trimethoxy-silane, and the whole was stirred
 35 for 48 hrs at room temperature. After all volatile constituents

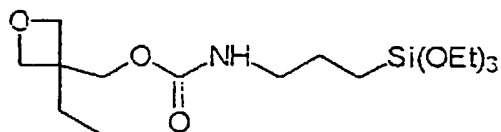
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had been removed by drying at 60°C at 0.1 mbar, 30 g (81% yield) of a colourless liquid were obtained.

¹H-NMR: 4.2-4.5 (m, 6H, CH₂O), 3.6 (s, 9H, CH₃O), 2.3-2.9 (m, 6H, CH₂S, CH₂C=O), 1.6-1.0 (m, 4H, CH₂), 0.8-1.0 (t, 3H, CH₃), 0.6-0.7 (t, 2H, CH₂Si) ppm.

IR (Film): 2940, 2870, 1737, 1459, 1244, 1089 cm⁻¹.

10 Example 2: Synthesis of N-(3-triethoxysilylpropyl)-(3-ethyloxetan-3-yl)-methyl carbamate (9)



(9)

15 11.6 g (0.1 mol) of 3-(3-ethyloxetanyl)methanol were added under argon in a dry apparatus to 24.7 g (0.1 mol) of 3-isocyanatopropyl triethoxysilane and 25 ml of anhydrous ether. After 20 mg of dibutyltin dilaurate had been added, the mixture
20 was stirred for 6 hrs at room temperature. After the solvent had been drawn off, 30 g (ca 85%) of a colourless liquid remained.

Elemental analysis:

25 C₁₆H₃₃NO₆Si [363.5] Calc.: C 52.86 H 9.15 N 3.85
Found: C 51.52 H 9.48 N 3.76

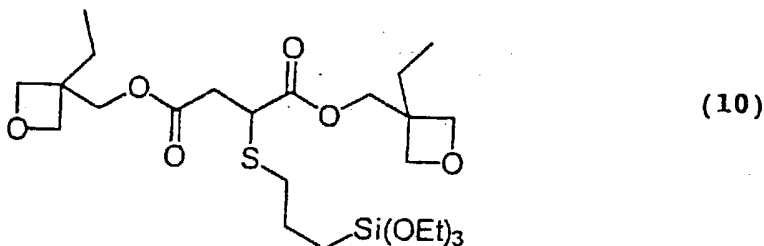
¹H-NMR: 5.6 (br, H, NH), 4.4-4.5 (q, 4H, CH₂O), 4.2 (s, 2H, CH₂O), 3.6-3.8 (q, 6HCH₂O), 3.0-3.3 (q, 2H, CH₂N), 1.4-1.8 (m, 4H, CH₂), 1.1-1.3 (t, 9H, CH₃), 0.9 (t, 3H, CH₃), 0.4-0.7 (t, 2H, CH₂Si) ppm.

IR (Film): 3336, 2972, 2930, 2880, 1724, 1533, 1245, 1080 cm⁻¹.

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Example 3: Synthesis of 2-(3-triethoxysilylpropylthio) succinic acid-bis-[(3-ethyloxetan-3-yl)-methyl] ester (10)



8.4 g (26.9 mmol) of fumaric acid-bis-[(3-ethyloxetan-3-yl)methyl] ester, 5.3 g (26.9 mmol) of 3-mercaptopropyltriethoxysilane and 0.33 g (1.3 mmol) of dibenzoyl peroxide were stirred for 5 hours in 20 ml of toluene at 100° C. When the solvent was distilled off, a white deposit precipitated which produced 10.2 g (70% yield) of (10) after filtering off and drying.

Example 4: Preparation of a Silicic Acid Condensate Based on Silane (8)

20 mmol of silane (8) and 20 mmol of dimethyldimethoxysilane were dissolved in 50 ml of anhydrous ethanol. After a mixture of 50 mmol of water and 5 ml of ethanol and some drops of 0.1 molar ethanolic acetic acid solution had been added, the whole was heated under reflux for 5 hours and was stirred overnight. After removal of volatile components in vacuo, the formed resin (7 g) could be used for a cationic polymerization.

Example 5: Preparation of a Dental Bonding

70 mg, i.e. 1 wt. %, of CYRACURE™ UVI 6974 photoinitiator was added to a mixture of 4g of resin from Example 4 and 3 g of 3,7-bis(3-oxetanyl)-5-oxanonane (3). The mixture was then cast as a film and irradiated for 60 s in a HELIOMAT™ dental irradiation device (HELIOMAT is a trade-mark of Etablissement Vivadent Corporation). A solid, well adhering film formed.

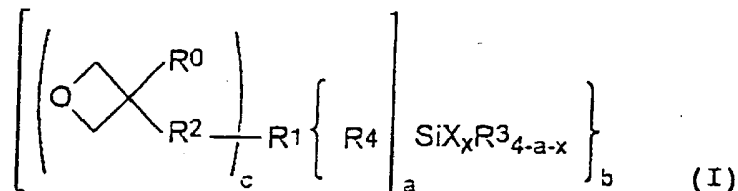
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5 The densities of the starting resin and the polymerisate were determined in each case according to the buoyancy method, the change in volume, i.e. the shrinkage, during the cationic ring-opening polymerisation being given by the density difference. The obtained ΔV value of only -4.1% was clearly lower than that for conventional bondings based on methacrylate. For example, the volume shrinkage during the curing of the commercially available HELIOBOND™ bonding agent is 7.5% (HELIOBOND is a trade-mark of Etablissement Vivadent Corporation).

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CLAIMS:

1. Hydrolysable and polymerizable oxetane silanes of the general formula (I) and stereoisomers thereof



in which the variables R^0 , R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , X , Y , a , b , c , and x , unless otherwise stated, independently of one another, have the following meanings:

R^0 = hydrogen or C_1 to C_{10} alkyl;

R^1 = missing or represents C_1 to C_{18} alkylene, C_6 to C_{18} arylene, C_7 to C_{18} alkylenearylene or arylenealkylene, these radicals being able to be interrupted by at least one group selected from ether, thioether, ester, carbonyl, amide and urethane groups;

R^2 = missing or represents C_1 to C_{18} alkylene, C_6 to C_{18} arylene, C_7 to C_{18} alkylenearylene or C_7 to C_{18} arylenealkylene, these radicals being able to be interrupted by at least one group selected from ether, thioether, ester, thioester, carbonyl, amide and urethane groups or being able to bear these in the terminal position;

R^3 = missing or represents C_1 to C_{18} alkyl, C_2 to C_{18} alkenyl, C_6 to C_{18} aryl, C_7 to C_{18} alkylaryl or C_7 to C_{18} arylalkyl, these radicals being able to be interrupted by at least one group selected from ether, thioether, ester, carbonyl, amide and urethane groups;

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R^4 = represents $-\text{CHR}^6-\text{CHR}^6-\text{S}-\text{R}^5$, $-\text{S}-\text{R}^5-$ or $-\text{Y}-\text{CO}-\text{NH}-\text{R}^5$;

R^5 = C_1 to C_{18} alkylene, C_6 to C_{18} arylene, C_6 to C_{18} alkylenearylene or C_6 to C_{18} arylenealkylene, these radicals being able to be interrupted by at least one group selected from ether, thioether, ester, carbonyl, amide and urethane groups;

R^6 = hydrogen or C_1 to C_{18} alkyl or C_6 to C_{10} aryl;

X = a hydrolysable group, namely halogen, hydroxy, alkoxy or acyloxy;

Y = O or S;

a = 1, 2 or 3;

b = 1, 2 or 3;

c = 1 to 6; and

x = 1, 2 or 3;

and with the proviso that

(i) $a+x = 2, 3$ or 4

and

(ii) a and/or $b = 1$.

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2. Oxetane silanes according to claim 1, wherein R^0 is substituted one or more times by substituents selected from the group consisting of methyl, ethyl, phenyl, benzyl, hydroxymethyl, hydroxyethyl, methoxy, ethoxy, chloro, bromo, hydroxy, mercapto, isocyanato, vinyloxy, acryloxy, methacryloxy, allyl, styryl, epoxy, carboxyl, SO_3H , PO_3H_2 or PO_4H_2 .
3. Oxetane silanes according to claim 1 or 2, wherein R^1 is substituted one or more times by substituents selected from the group consisting of methyl, ethyl, phenyl, benzyl, hydroxymethyl, hydroxyethyl, methoxy, ethoxy, chloro, bromo, hydroxy, mercapto, isocyanato, vinyloxy, acryloxy, methacryloxy, allyl, styryl, epoxy, carboxyl, SO_3H , PO_3H_2 or PO_4H_2 .
4. Oxetane silanes according to any one of claims 1 to 3, wherein R^2 is substituted one or more times by substituents selected from the group consisting of methyl, ethyl, phenyl, benzyl, hydroxymethyl, hydroxyethyl, methoxy, ethoxy, chloro, bromo, hydroxy, mercapto, isocyanato, vinyloxy, acryloxy, methacryloxy, allyl, styryl, epoxy, carboxyl, SO_3H , PO_3H_2 or PO_4H_2 .
5. Oxetane silanes according to any one of claims 1 to 4, wherein R^3 is substituted one or more times by substituents selected from the group consisting of methyl, ethyl, phenyl, benzyl, hydroxymethyl, hydroxyethyl, methoxy, ethoxy, chloro, bromo, hydroxy, mercapto, isocyanato, vinyloxy, acryloxy, methacryloxy, allyl, styryl, epoxy, carboxyl, SO_3H , PO_3H_2 or PO_4H_2 .
6. Oxetane silanes according to any one of claims 1 to 5, wherein R^4 is substituted one or more times by substituents selected from the group consisting of methyl, ethyl, phenyl, benzyl, hydroxymethyl, hydroxyethyl, methoxy, ethoxy, chloro, bromo, hydroxy, mercapto, isocyanato, vinyloxy, acryloxy, methacryloxy, allyl, styryl, epoxy, carboxyl, SO_3H , PO_3H_2 or PO_4H_2 .

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7. Oxetane silanes according to any one of claims 1 to 6, wherein R^5 is substituted one or more times by substituents selected from the group consisting of methyl, ethyl, phenyl, benzyl, hydroxymethyl, hydroxyethyl, methoxy, ethoxy, chloro, bromo, hydroxy, mercapto, isocyanato, vinyloxy, acryloxy, methacryloxy, allyl, styryl, epoxy, carboxyl, SO_3H , PO_3H_2 or PO_4H_2 .
8. Oxetane silanes according to any one of claims 1 to 7, wherein R^6 is substituted one or more times by substituents selected from the group consisting of methyl, ethyl, phenyl, benzyl, hydroxymethyl, hydroxyethyl, methoxy, ethoxy, chloro, bromo, hydroxy, mercapto, isocyanato, vinyloxy, acryloxy, methacryloxy, allyl, styryl, epoxy, carboxyl, SO_3H , PO_3H_2 or PO_4H_2 .
9. Oxetane silanes according to any one of claims 1 to 8, wherein at least one of the variables of formula (I), unless otherwise stated, independently of the other variables, has the following meaning:

R^0 = hydrogen or C_1 to C_5 alkyl;

R^1 = C_1 to C_8 alkylene, these radicals being able to be interrupted by at least one group selected from ether, thioether, ester and urethane groups;

R^2 = missing or represents C_1 to C_8 alkylene, these radicals being able to be interrupted by at least one group selected from ether, thioether, ester, thioester, carbonyl, amide and urethane groups or being able to bear these in the terminal position;

R^3 = missing or represents methyl, ethyl or phenyl;

R^4 = missing or represents - $S-R^5$ - or - $Y-CO-NH-R^5$;

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R^5 = C_1 to C_8 alkylene, these radicals being able to be interrupted by at least one group selected from ether, thioether, ester, carbonyl, amide and urethane groups;

R^6 = hydrogen or C_1 to C_5 alkyl;

X = methoxy, ethoxy or chloro;

Y = O or S;

a = 1;

b = 1;

c = 1 to 6;

x = 2 or 3; and/or

$a+x$ = 3

10. Oxetane silanes according to any one of claims 1 to 9, where in formula (I), unless otherwise stated, independently of the other variables, at least one of the variables, a , b and c = 1.
11. Polymerizable silicic acid condensates of the oxetane silanes according to any one of Claims 1 to 10, which are obtainable by hydrolysis and condensation of the oxetane silanes (I).

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12. Polymerizable silicic acid condensates of the oxetane silanes according to any one of Claims 1 to 10, which are obtainable by hydrolysis and condensation of the oxetane silanes (I) in the presence of other hydrolysable compounds.
13. Polymers of the oxetane silanes according to any one of claims 1 to 10 or of the silicic acid condensates according to claim 11 or 12.
14. Compositions containing the oxetane silanes according to any one of claims 1 to 10 or the silicic acid condensates according to claim 11 or 12.
15. Compositions according to claim 14, which contain
 - (a) 5 to 90 wt.%, relative to the composition, of silicic acid condensate according to claim 11 or 12,
 - (b) 0 to 80 wt. %, relative to the composition, of diluent monomer,
 - (c) 0.1 to 5 wt. %, relative to the composition, of polymerization initiator, and
 - (d) 0 to 90 wt. %, relative to the composition, of fillers.
16. Compositions according to claim 15, which contain 10 to 70 wt.%, relative to the composition, of silicic acid condensate.
17. Compositions according to claim 15 or 16, which contain 0 to 50 wt.%, relative to the composition, of diluent monomer.
18. Compositions according to any one of claims 15 to 17, which contain 0.2 to 2.0 wt.%, relative to the composition, of polymerization initiator.

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19. Compositions according to any one of claims 15 to 18, which contain 0 to 80 wt.%, relative to the composition, of fillers.
20. Use of the oxetane silanes according to any one of claims 1 to 10, of the silicic acid condensates according to claim 11 or 12, of the polymers according to claim 13 or of the compositions according to any one of claims 14 to 19, as dental material or as a constituent of dental material.